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REPORT

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U.S. Army Toxic and Hazardous
Materials Agency

Documentation of the Development and Certification of an Analytical Method for Determination of HD in Soils and Concrete

by

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Advanced Development and Field Testing of Novel Processes to Decontaminate Chemical Agent Contaminated Facilities

TASK ORDER NO. 3
Demonstration of Hot Gas Decontamination System for Chemical Agents

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The method involves liquid-solid extraction of the matrix using chloroform with a vortex mixer followed by filtering. The analyte is determined using capillary gas-liquid chromatography (GC)/flame photometric detector (FPD) in sulfur mode (393-nm pass filter). The chromatographic peak is integrated using a computerized data system with data storage capabilities.

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Documentation of the Development and Certification of an Analytical Method for Analysis of HD in Soils and Concrete

I. SUMMARY

A. GENERAL METHOD. The method involves liquid-solid extraction of the matrix using chloroform with a vortex mixer followed by filtering. The analyte is determined using capillary gas-liquid chromatography (GC)/flame photometric detector (FPD) in sulfur mode (393-nm pass filter). The chromatographic peak is integrated using a computerized data system with data storage capabilities.

B. MATRIX. This method is suitable for the determination of HD in finely-divided concrete or soil.

C. ANALYTE. Sulfur mustard (HD) can be determined using this method.

II. APPLICATION

A. TESTED CALIBRATION RANGE. For a 10-g soil sample extracted with 10 mL of a chloroform solution, in which butyl sulfide has been added at a 1-mg/mL concentration, a 2-μL aliquot is injected. This method was found to be suitable for determination of HD over the range of 0.095-19 μg/mL or 0.095-19-μg/g soil. The calibration data does conform to a cubic regression analysis which has been performed using the logarithm of both the x and y-axis values. This is the typical method of handling data using the sulfur mode of a FPD.

B. SENSITIVITY. The response of the FPD at 393 nm for HD was estimated at 127 integrated area units per 1.0-μg HD for the instrumental setup as described at the certified reporting limit given below.

C. REPORTING LIMIT. The certified reporting limit (CRL) for the complete analytical method determined from the found versus actual concentrations for spiked standard matrix samples as defined by the USATHAMA QA/QC program (PC version 1 April 1988) is 1.79-μg HD/g soil. This was determined using 10-g soil, extracted with 10-mL chloroform solution, and a 2-μL splitless injection.

D. INTERFERENCES. The method was certified using USATHAMA-supplied standard soil for both matrices. During the certification process no interferences were observed. The analysis method promises to be very selective for HD since both a highly selective separation technique and a detector specific for sulfur have been used. The only interferences that may be observed using this method are extremely large quantities of sulfur-containing compounds eluting from the GC column near HD. The degradation products from mustard, including oxathiane, dithiane, and thiodiglycol, are a possible source of these interference compounds. The method has been tested with a 100:1 ratio of these common degradation products to mustard

with no observed problems. Since this level of contamination is in excess of that expected for most applications with soil or concrete, the method not suffer from interference problems due to these compounds is not expected.

E. ANALYSIS RATE. The analysis rate is variable depending upon the chromatographic conditions. Using the conditions recommended in this report, the extraction and analysis of the samples can be performed at the rate of 15 samples per 24-hr period.

F. SAFETY INFORMATION

1. Exempt Mustard. The hazards from exempt mustard (XH) or exempt distilled mustard (XHD) are primarily that of liquid XH or XHD contact with any part of the body. The most sensitive tissues are the eyes and mucous membranes. Moist tissues seem to have a greater reaction than do dry tissues. A secondary hazard exists from exposure to the vapors. While vapors from spills can cause irritation to the membrane which surrounds the eye, mechanically-generated vapors can damage the respiratory system and do permanent damage to the eyes. With chronic exposure, sensitization to the material occurs in most individuals. The International Agency for Research on Cancer has identified mustard as a human carcinogen.

   a. Mechanism of Action and Physiologic Effects. The hazard comes from the ability of these materials to act as vesicating agents. They enter the body tissues and act at the molecular level as alkylating agents. This results in burns. The degree of the burn depends upon the concentration and length of time that the tissues are exposed. While XHD will normally only cause a minor first degree burn (redness of the skin) after skin contact, severe irritation to the membrane around the eye and likely permanent damage to the eye can result if small amounts are allowed to remain in contact with the eyes. Second degree burns are likely if additional contributing factors such as increased concentration by evaporation of the solvent or if clothing or other barriers will not allow the material to evaporate normally. Second degree burns are likely if sensitization or areas of increased sensitivity (mucosal membranes or moist tissues) are involved. Under extreme conditions with contributing factors, third degree burns are feasible.

   b. Specific Toxic Effects. The mustards XH or XHD have been identified as a human carcinogen. Because these effects are cumulative and manifestations of injury are often delayed for a long time (10 - 20 years), both acute and chronic exposures to even low levels of these mustards are considered to be a health hazard. Mustard is an insidious

agent. The agent's odor (which is detectable at about 0.001 mg/m^3) quickly becomes unnoticeable after the first detection because it causes the olfactory nerves to become insensitive. Another indication of the insidiousness is the absence of pain for a period possibly hours after liquid or vapor contact with the skin, and for many minutes even after eye contact with the liquid.

2. Reagents

a. Chloroform (Trichloromethane) (CAS 67-66-3, N XX3). Chloroform reacts with active metals and strong alkaline solutions. Toxic and corrosive gases are formed on contact with flames or hot glowing surfaces. Hazardous decomposition products are phosgene, hydrogen chloride, and chlorine. Chloroform is a suspected carcinogen and a known mutagen. It is hazardous through inhalation, skin absorption, and ingestion. Following acute exposure, death may occur from cardiac arrest or hepatic damage.

b. Hexane (CAS 110-54-3, N 174). Hexane is a highly volatile, flammable liquid producing CO and CO_2 when combusted. Prolonged contact with the skin can cause moderate irritation, defatting, and dermatitis. Excessive inhalation of vapors produces nasal and respiratory irritation, headache, nausea, dizziness, possible unconsciousness, and even asphyxiation. Swallowing this compound can cause gastrointestinal irritation, nausea, diarrhea, and vomiting. Aspiration of hexane into the lungs can cause chemical pneumonitis which can be fatal. Repeated exposure may damage peripheral (arms and legs) nerve tissue and result in muscular weakness and loss of sensation in the extremities.

c. Dibutyl Sulfide (CAS 544-40-1). Dibutyl sulfide has a strong stench and is an irritant to skin and mucous membranes.

d. Sodium Hypochlorite (Bleach) (CAS 7681-52-9, N 3544 & 1256). Bleach causes burns on the eyes and skin. Breathing a mist can cause damage to nasal and respiratory passages. Swallowing bleach can result in damage to the throat and esophagus. Avoid contact with strong mineral acids. Hazardous decomposition products are hypochlorous acid, chlorine, hydrochloric acid, and sodium chlorate.

e. Acetone. Acetone is a flammable liquid that must be handled as a solvent with a dangerous fire risk. The flash point (open cup) of acetone is -9.4°C, with an autoignition temperature of 537°C. The 1988-1989 ACGIH TLV for acetone is 750 ppm as an 8-hr TWA and 1000 ppm as a 15-min STEL. Acetone can be narcotic in high concentrations.

III. APPARATUS AND CHEMICALS

A. GLASSWARE AND HARDWARE

1. Pasteur pipettes, disposable, and filling device
2. GC autosampler vials
3. Screw-cap vials, glass 4 dram, disposable
4. Teflon cap-liners for 4-dram vials
5. Precision syringes
6. Syringe with luer tip attachment for sample filtering apparatus
7. Analytical balance capable of weighing 10 ± .01 g
8. Weighing equipment (weighing paper, calibration weights, spatulas, etc.)
9. Latex rubber gloves, disposable
10. Kimwipes/soft cotes
11. Microwipes
12. Pyrex baking dish
13. Wash bottle to contain bleach decontamination sclution
14. 4-L polypropylene beaker
15. Autosampler syringes - Hamilton liquid syringe, 10 μL
16. Vortex mixer
17. Recirculating refrigerated bath
18. Syringe filters for luer lock syringe 0.45-μm Gelman SR, disposable
19. Volumetric flasks - 10, 25, 100, and 1000 mL

B. INSTRUMENTATION

1. GC. Hewlett Packard Model 5890A GC, or equivalent, configured with either a FPD equipped with a 393-nm pass filter or a detector with equivalent sensitivity and specificity for HD.

   a. Instrument Parameters. The following conditions have been found to be suitable for exempt chemical surety materiel (XCSM) analysis within our laboratory. They should be considered as a guideline; the operational conditions selected for certification are to be those found to be optimal for the chromatographic system.

   Capillary Column: 0.32-mm ID x 30-m long
   Stationary Phase: Carbowax 20M 1.0-μm film thickness
   Carrier: Helium
   Temperature Program: 50°C (1.0 min) → 210°C @ 10°C/min
   Linear Velocity: 35 cm/sec
   Injection Volume: 2-μL splitless
   Injector Temp: 200°C
   Detector Temp: 200°C
   Detector Gas Flows: Air = 130 mL/min
   Hydrogen = 130 mL/min
   Oxygen = 15 mL/min

2. Autosampler. Hewlett Packard 7673A automatic sample injector or equivalent is recommended for the GC to provide better reproducibility and permit unattended injection of samples. The sample tray associated with the autosampler is to be cooled to < 10°C using a refrigerated, recirculating bath to maintain sample integrity.

3. Integrator. The analog signal from the detector is to be recorded using an electronic data system equipped with printer/plotter and data archival capabilities. A computerized laboratory data system equipped with appropriate chromatographic and statistical software or equivalent is recommended for GC data acquisition and processing. The laboratory data system needs to provide the capability for acquisition of the analog signal from the detector, peak integration, and storage. The data storage device, if used for long term archiving of the data from the GC analysis, should be a magnetic taping system. Computerized integration software is recommended to integrate either the chromatographic peak area or peak height for quantitation. The chromatographic integration software must be capable of indicating the parameters used in the integration of the peaks. These parameters are to include as a minimum the beginning and ending integration times and the position of the baseline.

C. ANALYTES

1. Mustard Bis(2-Chloroethyl sulfide) (HD)
   Boiling point: 217°C
   Melting point: 14°C
   Density: 1.27 g/mL @ 20°C
   CAS 505-60-2, 39472-40-7, or 68157-62-0

2. Dibutyl Sulfide (BS)
   Boiling point: 182°C
   Melting point: -79.7°C
   Density: 0.8316 g/mL @ 16°C
   CAS 544-40-1

D. REAGENTS AND SARMS

1. Reagents

   a. Decontamination Material. Sodium Hypochlorite (5 percent available chlorine in water).

2. Solvents

   a. Hexane (ACS) - Glass-distilled, UV spectrometric grade

   b. Chloroform (ACS) - Glass-distilled, UV spectrometric grade

c. Distilled deionized water

d. Acetone - Glass-distilled, UV spectrometric grade

3. SARMS

a. Soil - Provided by USATHAMA for certification and quality control samples. The soil is used as received, and any interferences observed as a result of its usage reported to the USATHAMA technical representative. The SARM soil sample is used to represent concrete for the method certification process.

b. XHD - Provided by USATHAMA for certification and preparation of calibration standards ≈ 5 mg/mL in chloroform.

IV. CALIBRATION

A. INITIAL CALIBRATION

1. Preparation of Standards. All standards including pre-certification and routine calibration standards are to be prepared using dilute solutions of SARM material. The XHD SARM stock provided by USATHAMA and used for our certification analyses is 4.75 ± 0.04 mg/mL. All example calculations will be made based upon the use of this stock. The preparation of all calibration solutions is to be conducted with precision syringes and volumetric glassware. The recommended procedures for the use of these items is provided below. In some cases the concentrations will not exactly be a whole number, but the use of volumes that can be accurately measured is of more importance than actually making the concentrations of the solutions a whole number. The actual concentration is reported to three significant digits.

CALIBRATION STANDARDS

Standard	Aliquot (μL)	Size of Volumetric Flask (mL)	Solution Concentration (μg/mL) HD
A	100•	25	19.0
B	50•	25	9.50
C	20•	25	3.80
D	1000*	10	1.90
E	1000**	10	0.950
F	1000***	10	0.380
G	100*	10	0.190
H	100**	10	0.0950
I	0.0	25	0.000

•Aliquot of USATHAMA SARM stock (4.75 ± 0.04-mg/mL)
*Aliquot of Standard A
**Aliquot of Standard B
***Aliquot of Standard C

a. Cleaning of Volumetric Glassware. Before use, volumetric glassware must be washed with a warm solution of detergent and, if necessary, cleaning solution. Fill with liquid to about one-third of its capacity. While holding it nearly horizontal, carefully rotate the glassware so that all interior surfaces are covered. Drain inverted and rinse thoroughly with distilled water. Only clean glass surfaces will support a uniform film of liquid; the presence of dirt or oil tend to cause breaks in this film. The appearance of water breaks is a certain indication of an unclean surface. Inspect for water breaks and repeat the cleaning cycle if necessary. Volumetric glassware is carefully cleansed by the manufacturer before being supplied with markings, and in order for these to have meaning, the equipment must be kept equally clean when in use.

As a general rule, the heating of calibrated glass equipment above 55°C should be avoided. Too rapid cooling can permanently distort the glass and cause a change in volume.

b. Use of Volumetric Glassware. All dilutions performed make use of volumetric glassware. Volumetric glassware is calibrated to contain a specified volume when filled to the line etched on the neck. If the XCSM is being measured as a volume, the appropriate size volumetric flask, as determined by final volume needed and calculation, must be filled approximately 75 percent full before initiation of XCSM transfer. The XCSM is transferred into the volumetric

flask as described in Section IV.A.1.c or IV.A.1.d. The XCSM must be transferred to the diluent in the volumetric flask with the tip of the transfer device held below the surface of the solvent to prevent evaporative loss of XCSM. The contents of the flask are swirled to achieve mixing. More solvent is added to the flask, and the solution is mixed well. The liquid level is filled almost to the mark allowing time for drainage. Use a small pipette or syringe to make such final additions of solvent as are necessary. For the most accurate work, the flask should be maintained at the temperature indicated on the volumetric glassware. The contents of the flask are mixed thoroughly again before dispersing.

NOTE: When a liquid is confined in a narrow tube such as a pipette or neck of a volumetric flask, the surface is found to exhibit a marked downward curvature called a meniscus. It is common practice to use the bottom of the meniscus in calibrating and using volumetric glassware. This minimum can often be established more exactly if an opaque card or a piece of paper is held behind the gradations.

c. Use of Pipettes. When XCSM is to be transferred with a pipette and aspirator bulb, the following procedures are to be followed. The operator will check the bulb attached to the pipette to ensure that the bulb is working properly. If there is any doubt as to the integrity of the bulb, a new one will be obtained and checked.

The XCSM will be drawn into the pipette until the desired quantity has been obtained. To do this, the tip of the pipette is placed below the surface of the XCSM. The operator aspirates the XCSM into the pipette using the pipette bulb. Once the XCSM has reached the desired level, the operator stops the aspiration May overfill slightly and adjust downward, but never allow liquid to enter bulb.

The outside of the pipette tip is wiped with a plastic-backed wipe as it is withdrawn from the primary container. The absorbent wipe is discarded into the decontamination beaker. The XCSM will be expelled into the receiving container using the pipette bulb. There are two types of pipettes commonly used for measuring liquids. The pipettes which deliver a fixed volume are called volumetric or transfer pipettes. These pipettes usually carry notation "TD" on outside surface. Other pipettes, known as measuring pipettes, are calibrated in convenient units so that any volume up to maximum capacity can be delivered. If the pipette used is a volumetric pipette, place the tip of the pipette well into the receiving vessel and allow the sample

to drain freely. When free flow ceases, rest the tip against the receiving vessel inner wall. Finally, withdraw the pipette with a rotating motion to remove any droplet adhering to the tip. The small volume remaining inside the tip is not to be blown or rinsed into the receiving vessel. In the case of color-coded pipettes, a frosted ring indicates complete blow out. Volumetric pipettes are never blown out.

After the volume of agent has been delivered in an agent operation, the transfer device used must be appropriately decontaminated.

d. Use of Syringes. When transfer is made with a precision syringe, such as those made by Hamilton, the following procedures are used. The syringe used must be an appropriate size so that the volume used can be accurately measured. It is desirable that the syringe be of a size such that the volume to be measured is greater than 50 percent of the total volume of the syringe. Be certain the syringe and plunger are clean before filling. To fill the syringe, place the tip of the syringe below the surface of the XCSM and aspirate the XCSM into the syringe. Care must be taken to avoid small air bubbles that can be trapped in the sample. To assure an accurate measurement, wet the interior surfaces (barrel and plunger) of the syringe with the sample by pumping the plunger before filling. When properly done, this neutralizes the liquid movement by capillary forces. Overfill the syringe in the XCSM vial, raise the syringe tip above the liquid surface, and then move the plunger to the desired calibration line. This is your best assurance of a full sample, since discharging the excess while the needle is still in the sample may result in a loss of sample upon withdrawing the needle from the liquid. Read the syringe gradation from the same angle each time you fill the syringe. Recommended practice is to read the sample at the "top" (flange end) of the calibration line. This provides an accurate visual check and reduces the problems of "line thickness." Strive to develop a smooth uniform loading operation to minimize slight involuntary errors. Syringes with detachable needles require care when filling because of the dead volume in the needle and potential air bubbles that form at the luer tip of a syringe.

As the syringe is withdrawn from the vial, the portion which came in contact with the XCSM is drawn through plastic-backed, absorbent paper taking care not to wipe sample out of the needle and not to transfer body heat from

your fingers to the needle. The plastic-backed, absorbent paper, upon completion of this step, is disposed of in the decontamination solution.

To dispense the sample, the needle of the syringe is carefully lowered into the receiving container, taking care not to touch the outside of the container with the needle. The tip is touched against the inside wall below the level of the solvent when dilutions are being prepared. The contents of the syringe are expelled into the container. The syringe is withdrawn from the dilution or transfer vessel and wiped carefully with a plastic-backed, absorbent pad as it is withdrawn. The syringe is placed on five layers of brown paper or plastic-backed, absorbent pad until proper decontamination procedures can be followed.

After the volume of XHD has been delivered in an XCSM operation, the transfer device used must be appropriately decontaminated. A syringe or similar glass and metal constructed apparatus must be decontaminated using solvents.

e. Internal Standard Spiking Solution. Dibutyl sulfide is used when samples are to be analyzed for H or HD. Prepare 100 mL of dibutyl sulfide spiking solution at 1-mg/mL concentration. To prepare this solution, place approximately 75-mL distilled-in-glass chloroform in a 100-mL volumetric flask and spike the chloroform with 120 μL of neat dibutyl sulfide.

Example calculations:

Dibutyl sulfide d = 0.8316 mg/μL
Final volume = 100 mL
Desired concentration = 1.0 mg/mL
1 μg/mL x 100 mL = 100 mg/100-mL chloroform
100-mg dibutyl sulfide/0.8316 mg/μL = 120 μL
Resulting concentration = 0.998 mg/mL

f. Standard Diluent. Prepare 1 L of standard diluent with internal standard. The appropriate stock internal standard spiking solution prepared in Section IV.A.1.e is used to spike the internal standard into the analytical standards. To prepare the standard diluent, place approximately 750 mL of distilled-in-glass chloroform in a 1-L volumetric flask. To the 750 mL of chloroform, add 1.00 mL of the internal standard spiking solution using a 1-mL precision syringe. The volumetric flask is mixed and filled and mixed again in accordance with Section IV.A.1.b. This standard diluent is used to prepare all standards and is used as the extraction solvent.

2. Instrument Calibration. The GC is calibrated with eight standard solutions plus a reagent blank solution. Duplicate injections of each standard over the concentration range of interest are sequentially injected into the GC in random order. Peak areas and peak heights are obtained for each analyte.

3. Analysis of Calibration Data. The linear model, assessed using the protocol specified in the USATHAMA QA Program (2nd Edition, March 1987), is not applicable to this analysis method. Experience indicates that a linear model is not practical using sulfur analyses with a FPD. The regression model that accommodates these data is a cubic regression analysis using the logarithm of the peak area ratio (HD/internal standard) and the logarithm of the concentration. Using this regression analysis procedure, the data has been found to fit the following equation:

$$y = (d + cx + bx^2 + ax^3),$$

where: x = ln of peak area; y = ln of actual nanograms of agent, and a, b, c, and d are the third order polynomial coefficients.

B. DAILY CALIBRATION. The daily calibration is performed using standards A through F described in Section IV.A.1 above. These standards are analyzed in duplicate at the beginning and end of the day (after last sample of the day). A regression analysis is performed using the peak areas obtained at the standard concentrations.

1. Preparation of Standards. The standards A through F plus I are prepared as described in Section IV.A.1 above.

2. Instrument Calibration. The instrument is calibrated following the same procedures as described in Section IV.A.2 above with the exception that standards G and H are not analyzed.

3. Analysis of Calibration Data. The data is analyzed as described in Section IV.A.3 above.

4. Calibration Checks. The average peak area ratio at each of the calibration concentrations is compared to the calibration analyses for each day. The found concentration must agree within 5 percent of the target value. If this is not observed, the problem must be resolved and a new calibration must be obtained before analysis of samples may resume.

V. CERTIFICATION TESTING

A. CERTIFICATION PROCEDURE. The certification of the analytical method is performed in accordance with the USATHAMA guidelines. The USATHAMA certification process requires that a SARM soil matrix be

challenged prior to extraction with a range of XHD SARM concentrations. The range and duration of the certification process is dependent upon the class of certification required. The different classes of certification and specific details are discussed within the USATHAMA QA Program manual. The certification process described within this report is for the Class 1 certification. The standard sample set used is the minimum testing range (MTR) +1 order of magnitude extension.

The certification period for a quantitative method has been defined by USATHAMA as 4 days. On each of the 4 certification study days, SARM soil samples are weighed and challenged with eight levels of SARM XCSM over the certification range. Each of the certification samples are prepared and extracted daily along with one process blank (non-spiked USATHAMA SARM soil) in accordance with Sections V.A.1 and VII.A below. The USATHAMA SARM soil has been substituted for the concrete matrix during the validation phase since SARM concrete has not yet been defined.

Over-spiked samples (samples prepared by challenging the unknown sample matrix with SARM XCSM), and QA samples (samples prepared by challenging the SARM soil matrix with SARM XCSM) are prepared using the procedures described in Section V.A.1 below. These samples are prepared and analyzed with each unknown sample set to provide method quality control information. The results of the over-spike and QA sample set are used in the control charting of the method.

1. Certification Sample Preparation. Prior to sample preparation, obtain an appropriate quantity of screw-cap, 4-dram vials with Teflon cap-liners to be used as extraction vials. The vials are to be labeled for XCSM samples. The quantity of vials necessary will depend upon the certification range selected. The MTR +1 order of magnitude extension range requires that nine samples be weighed, prepared, and analyzed each day.

   Weigh 10.0 ± 0.1 g of SARM soil into each labeled, screw-cap, 4-dram vial. Record the actual weights in a laboratory record book along with the laboratory sample identification number. The weighed samples contained in the extraction vials are transferred to a fume hood suitable for XCSM work.

   Remove the XHD SARM stock solution from the storage freezer and allow the solution to equilibrate to room temperature within the working hood. Once the stock solution has reached room temperature, the solution must be mixed thoroughly prior to use. Challenge each certification or over-spike sample matrix with the appropriate volume of the XHD SARM stock solution to provide the required range for certification samples.

Volumes of XCSM Necessary When a 4.75-mg/mL Stock is Used

Concentration in Extract Micrograms/Milliliter	Volume Stock Microliters	Concentration in Concrete Micrograms/Gram
0.00	0.0	0.0
0.095	2.0*	0.095
0.19	4.0*	0.19
0.38	8.0*	0.38
0.95	20.0*	0.95
1.9	4.0**	1.9
3.8	8.0**	3.8
9.5	20.0**	9.5
19.0	40.0**	19.0

*Volume calculated using a 1:10 dilution of SARM stock solution.
**Volume calculated using SARM stock solution without dilution.

Immediately after addition of the XHD material, the extraction vial is sealed and the matrix mixed by vortex mixer for 30 ± 5 sec to blend the XHD challenge with the sample matrix. Set vial aside within the working hood for 10 ± 0.5 min to permit the agent to interact with the sample matrix.

Repeat the process for all vials containing validation or over-spike sample matrix. After the 10-min wait period, the sample is extracted as described below in Section VII.A.

If the procedures followed during the certification process are modified during the unknown sample preparation and analysis phase, the entire process must be re-certified unless all modifications have been accepted by USATHAMA as insignificant to sample preparation or analysis.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE. Samples are collected per additional SOP. Samples must be stored in a cool (3 - 26°C) environment immediately after collection until extraction.

B. CONTAINERS. All containers used to store wet or dried soil should be cleaned according to procedures specified in the USATHAMA QA Manual.

C. STORAGE CONDITIONS. All soil samples are stored between 3° C and 26° C in their sealed containers until extracted.

D. HOLDING TIME LIMITS. Samples must be extracted within 30 days of receipt. The extracts are to be stored at -70° C. The extracts can be stored for at least 2 weeks at -70° C without measurable degradation of sample.

E. SAMPLE HOMOGENIZATION. Soil is mixed by shaking in a closed container or grinding in a mortar prior to weighing. The weighed sample should be from finely divided materials and not contain any large stones or particles.

VII. PROCEDURE

A. EXTRACTION. The following procedure is followed to obtain extracts from certification and QA samples of pulverized concrete or finely-divided soil. Prior to initiating the extraction procedure, the sample must be weighed into a 4-dram vial with Teflon-lined screw cap. The recommended sample weight for this extraction process is 10.0 ± 0.1 g of sample matrix.

All samples are extracted with 10.0 ± 0.1 mL of standard diluent prepared in Section IV.A.1.f. The standard diluent contains 1 ± 0.01-μg/mL butyl sulfide for the XH or XHD samples as an extraction/internal standard for the analysis method. After addition of the standard diluent, the vial is re-sealed and the matrices vortex mixed for 30 ± 5 sec. The vials are allowed to stand for 10 ± 0.5 min after mixing to provide separation of the liquid and solid phases. The addition of solvent and mixing is repeated for each of the remaining vials.

Once the phases have separated, an aliquot of the extract is withdrawn from the liquid phase of the extraction vial and filtered using a 0.45-μm syringe filter system. To filter the sample extract, attach one of the 0.45 μm filters to a clean gas tight syringe of at least a 2-mL volume. The plunger is removed and the sample extract placed into the syringe barrel using a disposable pipette. The syringe barrel should not be filled to greater than 75 percent of volume. The plunger is placed back into the syringe and the filtered extract expelled from the syringe through the filter into an appropriately labeled GC vial. Dispense 1.25 ± 0.25 mL of the filtrate into each of three labeled GC auto-sample vials. One vial is for GC analysis, one for possible GC/MS analysis, and one reserve sample. The transfer/filtering procedure is repeated for each of the samples remaining. Be careful to clean the syringe and replace the filter for each sample so that cross contamination does not occur. The extracts are stored at -70°C until analyses for XHD can be performed.

B. DETERMINATION. Determination of analyte concentrations in the extracts is accomplished by GC with 393-nm FPD. A 2-μL splitless injection is made onto a Carbowax capillary column. The retention time of HD is 6.7 ± 0.2 min and butyl sulfide is 5.9 ± 0.2 min using the instrument parameters described in Section III.B.1.a.

VIII. CALCULATIONS

A. CALIBRATION CURVE. Since a calibration curve is to be generated on a daily basis, the regression analysis will be performed each day to generate the regression parameters for the cubic regression equation:

$$y = d + cx + bx^2 + ax^3$$

The regression analysis is performed using the natural logarithms of the obtained peak area ratios ((HD peak area)/(BS peak area)) versus the (concentration). The regression analysis calculations using the calibration values for the range of standards analyzed will provide the parameter estimates for a, b, c, and d in the cubic regression equation.

B. ANALYTE CONCENTRATIONS. Solution concentrations (μg/mL) in the extracts (C_a) are then obtained by inserting the parameter estimates for a,b,c,and d into the following equation:

$$\ln C_a = d + cx + bx^2 + ax^3$$

where:

C_a = Concentration in extracts (μg/mL)
x = (peak area ratio)

The concentration in the sample (X_a), on a μg/g basis, is then obtained by multiplying the solution concentration by the volume of extraction solvent (10 mL) and dividing by the actual mass (M) of sample extracted (10 g recommended):

$$X_a = \frac{C_a(10.0)}{M}$$

IX. DAILY QUALITY CONTROL

A. CONTROL SPIKES. Spiked samples are prepared as described for Class 1 methods in the USATHAMA QA Program (2nd Edition, March 1987). This requires the use of a method blank, a single spike at two times the certified reporting limit, and duplicate spikes at ten times the certified reporting limit for each

analytical lot. Control spikes are prepared using the SARM solution in an identical manner as described in Section V.A.1 and extracted in accordance with Section VII.A.

B. CONTROL CHARTS. The control charts required are described for Class 1 methods in USATHAMA QA Program (2nd Edition, March 1987). This requires use of standard Shewhart X and R charts for the duplicate high spikes and moving average X and R charts for the single low spike. Details on the charting procedures required are specified in USATHAMA QA Program (2nd Edition, March 1987).

X. REFERENCES

USATHAMA (1987) USATHAMA QA Program, December 1985 (2nd Edition, March 1987). US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD 21010-5401.

XI. DATA

APPENDIX A - TABULATION AND GRAPH OF FOUND VERSUS TARGET CONCENTRATIONS

APPENDIX B - INITIAL CALIBRATION

The response versus concentration graphs are presented as Figures XI.B.1 and XI.B.2. Figure XI.B.1 shows the graphic result of plotting the calibration data as the peak area ratio versus target concentration. The graph clearly illustrates that this relationship is not linear. Figure XI.B.2 shows the graphic result of plotting the calibration data as the logarithm of the peak area ratio versus the logarithm of the target concentration. The resultant graph indicates that logarithmic relationship is linear. Thus, the use of the logarithm analyses for HD will be performed for all analyses.

APPENDIX C - STANDARD CERTIFICATION SAMPLES

APPENDIX A

TABULATION AND GRAPH OF FOUND VERSUS TARGET CONCENTRATIONS

TABLE XI.A.1. TABULATION OF FOUND VERSUS TARGET CONCENTRATION DATA, RESULTS OF LACK OF FIT, AND ZERO INTERCEPT TESTS

CERTIFICATION ANALYSIS — Report Date: 11/11/88

Method Name: SOIL/CONCRETE EXTRACTION — Laboratory: BC
Compound: HD — Analysis Date: 10/26/88
Units of Measure: UGG — Matrix: SO

ANALYSIS OF RESIDUAL VARIATIONS

	--- Model with Intercept --- Y = (-0.24226443) + (1.11548556)X			- Model through the Origin - Y = (1.09703980)X		
	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	11.06059500	30	0.36868650	12.29855020	31	0.39672743
Total Error:	7.563946000	24	0.315164417	7.563946000	24	0.315164417
Lack of Fit:	3.496649000	6	0.582774833	4.734604200	7	0.676372029

LOF F-Ratio(F): 1.849113677 — Critical 95% F: 2.51
LOF F-Ratio(F): 2.146092620 — Critical 95% F: 2.42

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted — Calculated F: 3.357744859 — Critical 95% F: 4.17

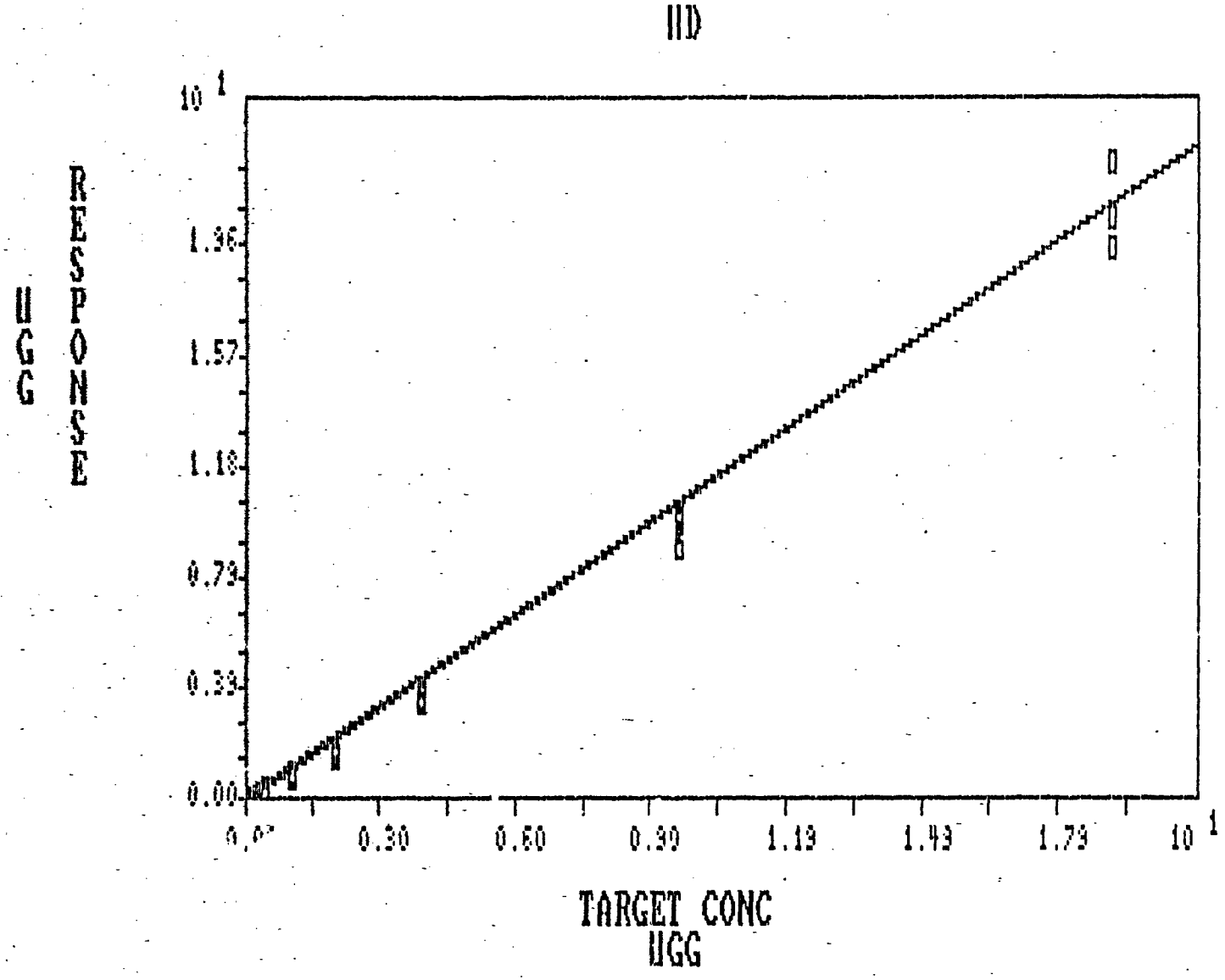
****

TABLE OF DATA POINTS — Targets: 8 — Measures per Target: 4

	Target Value	Found Concentration			
1:	0.0950000	0.1100000	0.0890000	0.1050000	0.1140000
2:	0.1900000	0.1600000	0.2060000	0.1910000	0.2180000
3:	0.3800000	0.3730000	0.3840000	0.3570000	0.3840000
4:	0.9500000	0.8930000	0.9250000	0.8620000	0.9330000
5:	1.9000000	1.6960000	1.4840000	1.7820000	1.8440000
6:	3.8000000	4.0560000	3.6940000	3.4670000	3.5590000
7:	9.5000000	9.5780000	9.9930000	10.105000	9.0890000
8:	19	22.600000	22.586000	20.591000	19.624000

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***

FIGURE XI.A.1. GRAPH OF FOUND VERSUS TARGET CONCENTRATIONS



APPENDIX B

INITIAL CALIBRATION

TABLE XI.B.1. RESPONSE VERSUS CONCENTRATION DATA

HD Concentration	HD Peak Area	BS Peak Area	HD/BS Ratio
0.00	0.00	116	0.00
0.00	0.00	122	0.00
0.00	0.00	128	0.00
0.00	0.00	129	0.00
0.095	0.683	115	0.006
0.095	0.645	114	0.006
0.190	2.47	114	0.022
0.190	2.83	112	0.025
0.380	10.6	112	0.095
0.380	10.7	111	0.097
0.950	64.4	107	0.601
0.950	65.9	108	0.610
1.90	278	110	2.53
1.90	274	109	2.52
3.80	1079	112	9.67
3.80	1076	111	9.66
9.50	6494	113	57.2
9.50	6189	107	58.0
19.0	19952	111	179
19.0	19863	110	180
0.095	1.00	132	0.008
0.095	0.730	125	0.006
0.190	3.75	126	0.030
0.190	3.86	126	0.031
0.380	13.0	120	0.109
0.380	13.2	122	0.108
0.950	83.9	129	0.652
0.950	85.0	130	0.656
1.90	337	130	2.59
1.90	327	126	2.61
3.80	1200	125	9.63
3.80	1246	130	9.61
9.50	7051	128	55.0
9.50	7047	128	55.1
19.0	20906	133	157
19.0	20928	134	156

FIGURE XI.B.1. HD ANALYSIS PAR VERSUS CONC. (*) WITH CUBIC REGRESSION (___) AND 95 PERCENT CONFIDENCE LIMITS (---)

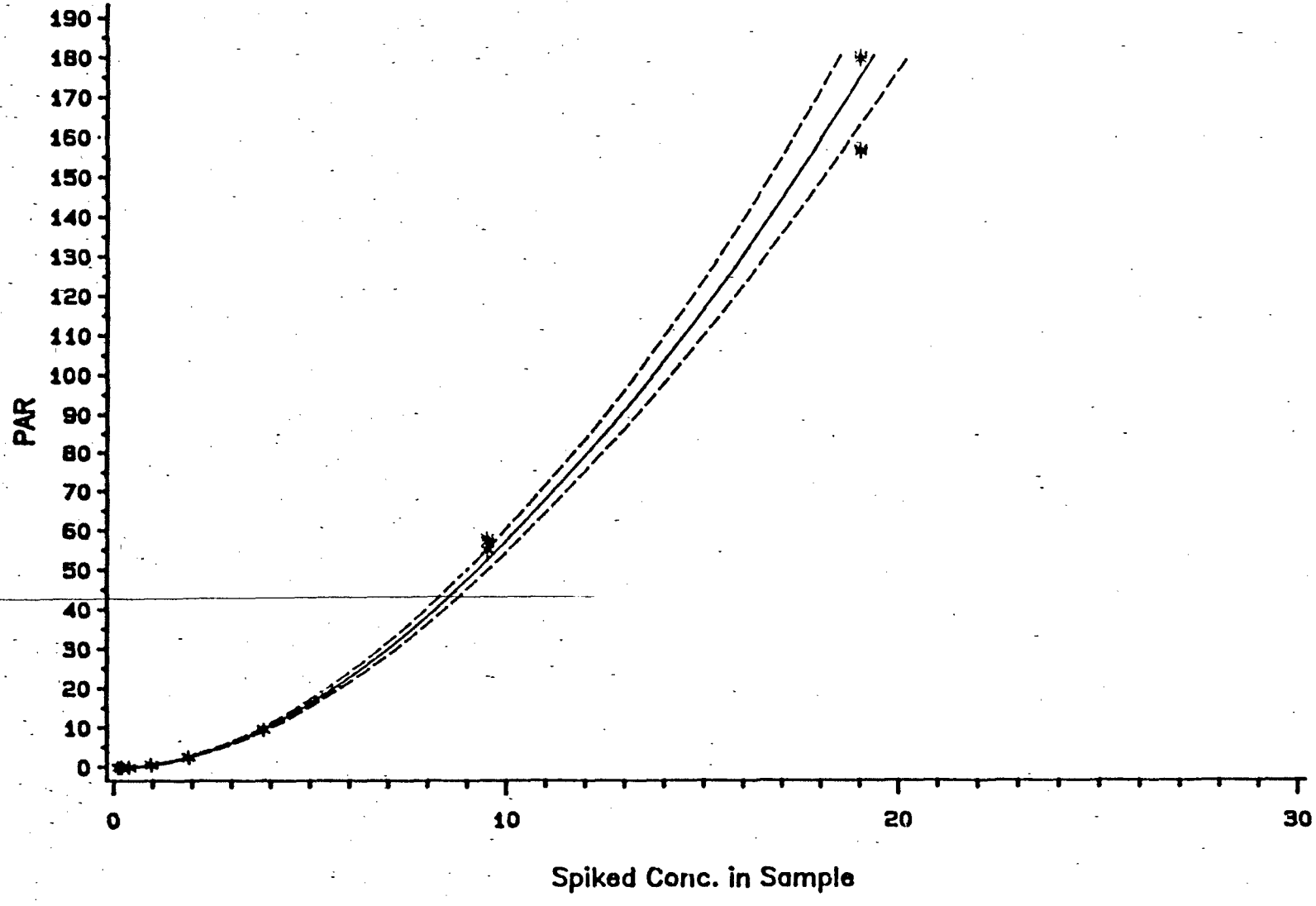
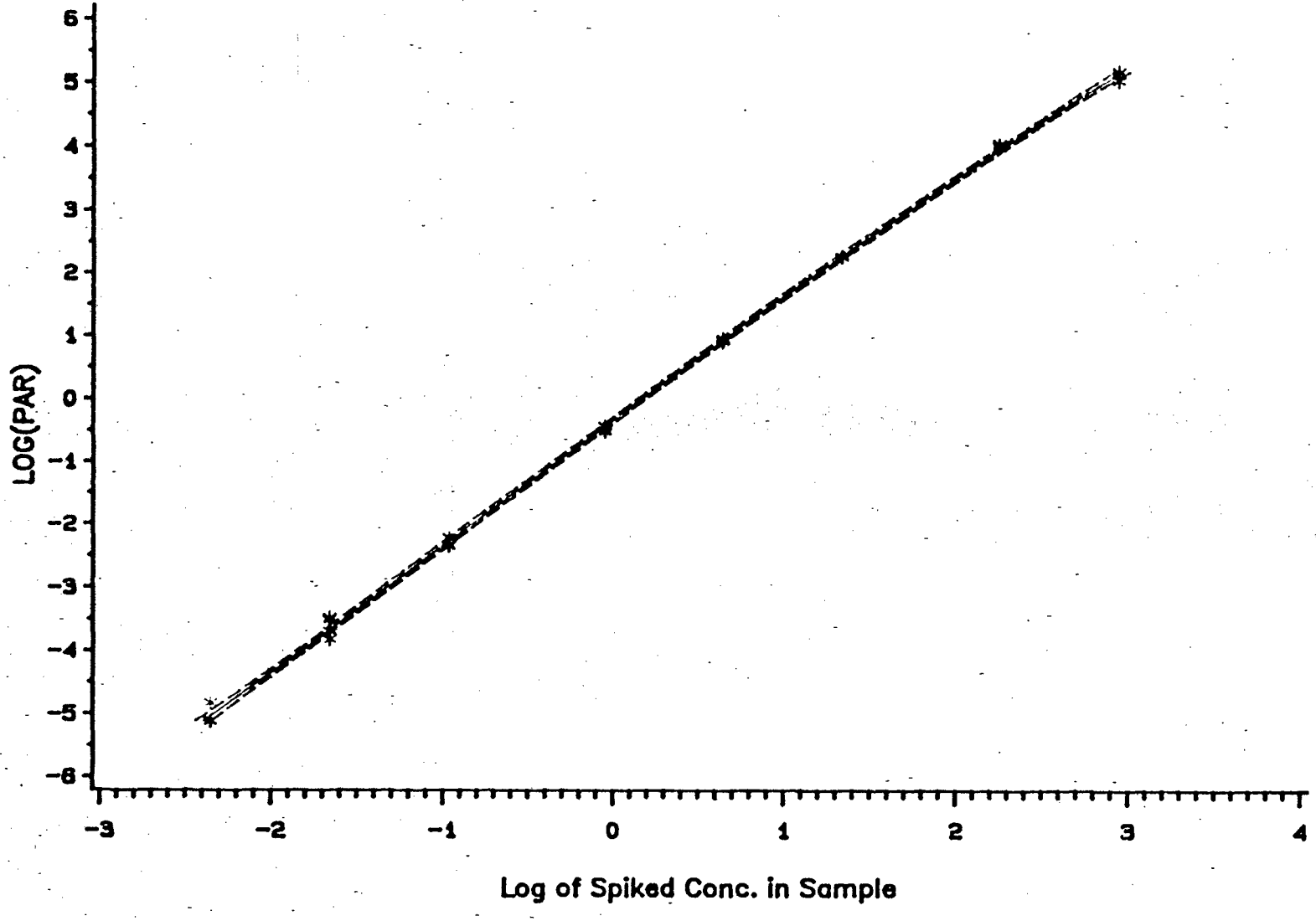


FIGURE XI.B.2. HD ANALYSIS LOG(PAR) VERSUS LOG(CONC.) (*) WITH CUBIC REGRESSION (___) AND 95 PERCENT CONFIDENCE LIMITS (---)



APPENDIX C

STANDARD CERTIFICATION SAMPLES

TABLE XI.C.1. TABULATION OF STANDARD DEVIATION, PERCENT INACCURACY, AND PERCENT IMPRECISION BY TARGET CONCENTRATION

CERTIFICATION ANALYSIS — Report Date: 11/11/88

Method Name: SOIL/CONCRETE EXTRACTION — Laboratory: BC
Compound: HD — Analysis Date: 10/26/88
Units of Measure: UGG — Matrix: SO

TABLE OF RESULTS FOR TRUNCATED DATA SET

Target Concentration	Standard Deviation	Percent Inaccuracy	Percent Imprecision
0.0750000	0.0109697	10	10.497278
0.1900000	0.0250649	1.9736842	12.936731
0.3800000	0.0127671	-1.447368	3.4091176
0.9500000	0.0324795	-4.921053	3.5958462
1.9000000	0.1571857	-10.44737	9.2381267
3.8000000	0.2587135	-2.789474	7.0036135
9.5000000	0.4610753	2.0131579	4.7576507
19	1.4383271	12.369737	6.9710055

TABLE XI.C.2. SUMMARY OF TARGET VERSUS FOUND CONCENTRATION DATA FROM CERTIFICATION ANALYSES

CERTIFICATION ANALYS 5 Report Date: 11/11/88

Method Name: SOIL/CONCRETE EXTRACTION Laboratory: BC
Compound: HD Analysis Date: 10/26/88
Units of Measure: UGG Matrix: SO

TABLE OF DATA POINTS

Target Concentration	Found Concentration
0	0
	0
	0
	0
0.0950000	0.1100000
	0.0890000
	0.1050000
	0.1140000
0.1900000	0.1600000
	0.2060000
	0.1910000
	0.2180000
0.3800000	0.3730000
	0.3840000
	0.3570000
	0.3840000
0.9500000	0.8930000
	0.9250000
	0.8620000
	0.9330000
1.9000000	1.6960000
	1.4340000
	1.7820000
	1.9440000
3.6000000	4.0560000
	3.6940000
	3.4670000
	3.5590000
9.5000000	9.5780000
	9.9930000
	10.105000
	9.0890000

TABLE XI.C.2.
(Continued)

CERTIFICATION ANALYSIS

Report Date: 11/11/88

Method Name:	SOIL/CONCRETE EXTRACTION	Laboratory:	BC
Compound:	HD	Analysis Date:	10/26/88
Units of Measure:	UGG	Matrix:	SO

TABLE OF DATA POINTS

Target Concentration	Found Concentration
19	22.600000
	22.536000
	20.591000
	19.624000

TABLE XI.C.3. CERTIFIED REPORTING LIMITS AND REGRESSION DATA

CERTIFICATION ANALYSIS — Report Date: 11/11/88

Method Name:	SOIL/CONCRETE EXTRACTION	Laboratory:	BC
Compound:	HD	Analysis Date:	10/26/88
Units of Measure:	UGG	Matrix:	SO

-- REGRESSION EQUATION --
Y = 1.1125451X + -0.203645

-- UPPER REPORTING LIMIT --
19

-- SLOPE --
1.1125451

SUMMARY TRUNCATION TABLE

Target Concentrations Used	Slope	% Change from Total Data Set	% Change from Previous Data Set
Entire data set	1.1125451	0	0
minus 1 highest	1.0177186	8.5233824	8.5233824
minus 2 highest	0.9594811	13.758004	5.7223601

Target Concentrations Used	Certified Reporting Limit	Upper Reporting Limit
Entire data set	1.7836569	19
Minus 1 highest	0.6743451	19
Minus 2 highest	0.6743451	19

FIGURE XI.C.1. GRAPH OF REGRESSION WITH CONFIDENCE BOUNDS OF FOUND VERSUS TARGET DATA

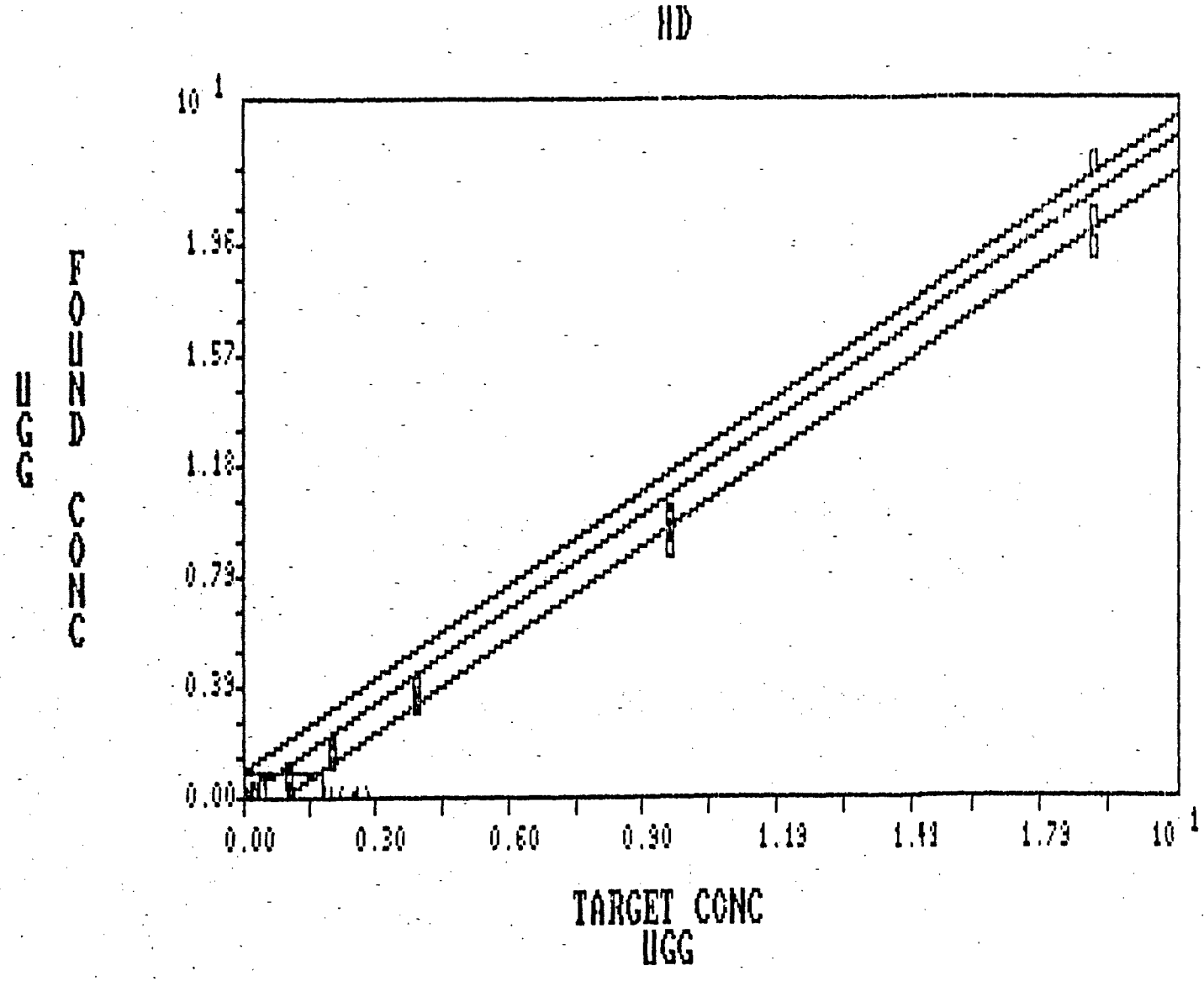
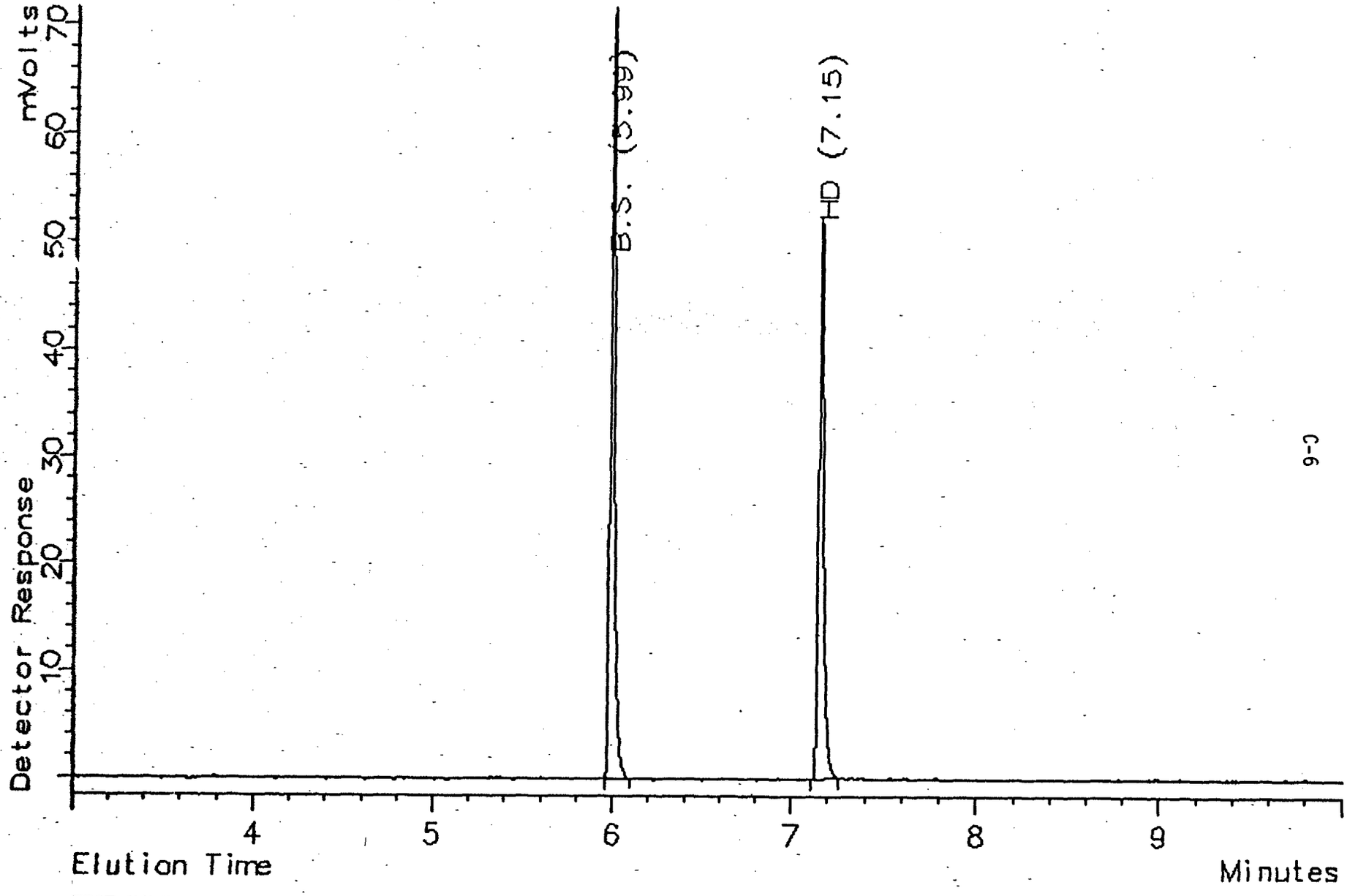


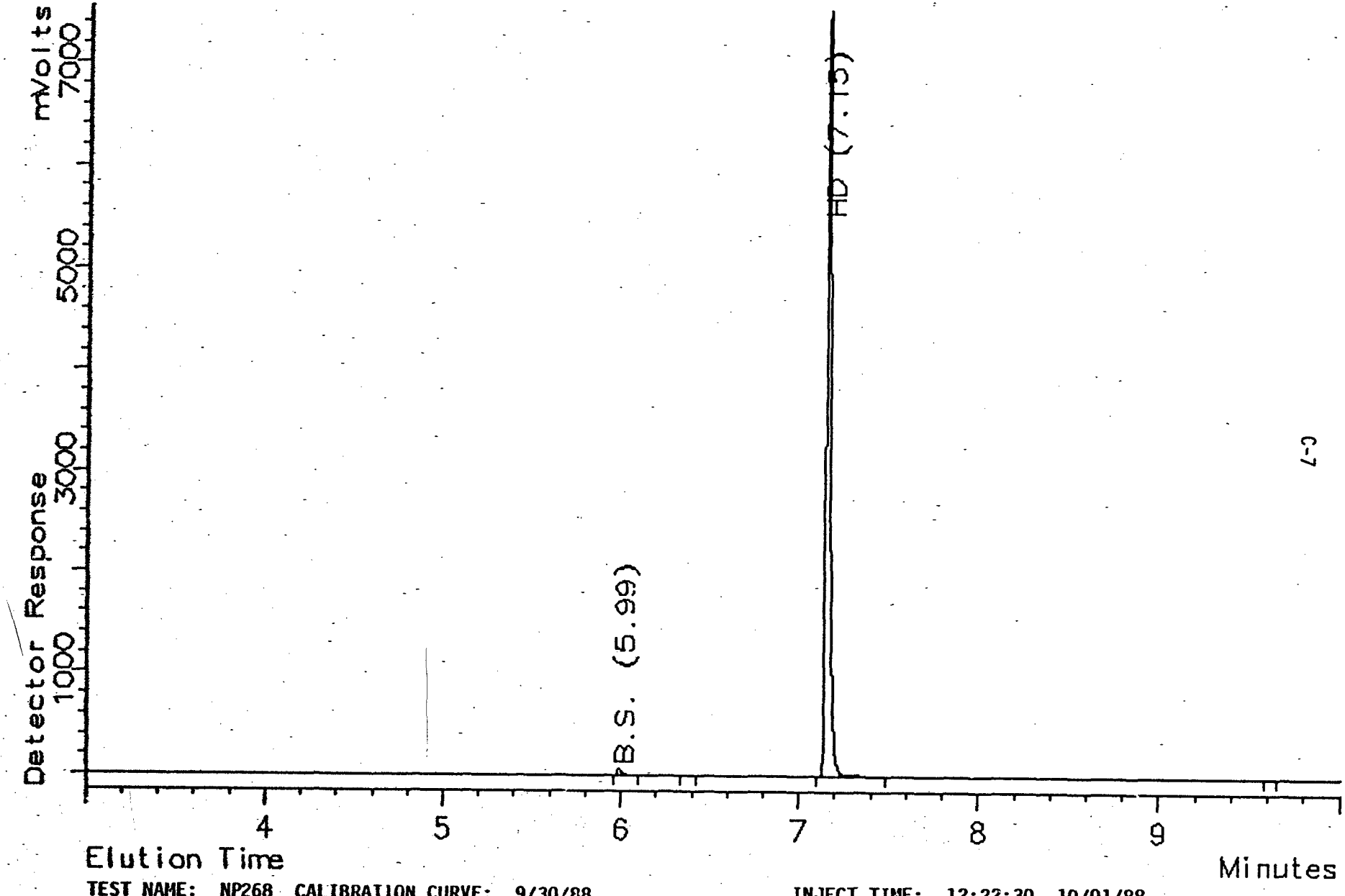
FIGURE XI.C.2. CHROMATOGRAM OF 1.90 ug/ml STANDARD ANALYSIS ON DAY 1



C-6

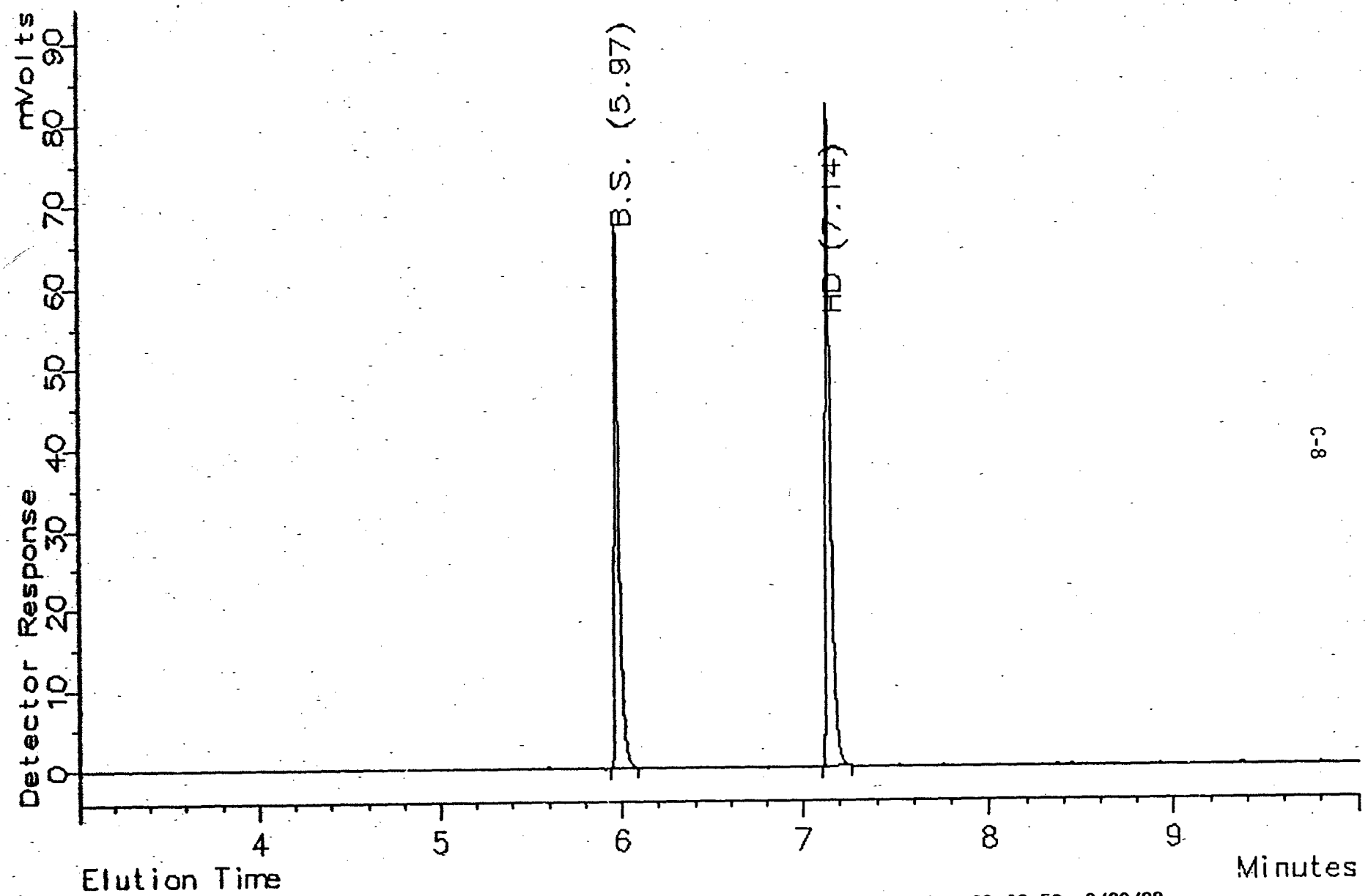
TEST NAME: NP262 CALIBRATION CURVE: 9/30/88 INJECT TIME: 17:59:17 9/30/88
GC0300 INSTRUMENT: 1

FIGURE XI.C.3. CHROMATOGRAM OF 19.0 ug/ml STANDARD ANALYSIS ON DAY 1



TEST NAME: NP268 CALIBRATION CURVE: 9/30/88 INJECT TIME: 12:22:30 10/01/88
GC0300 INSTRUMENT: 1

FIGURE XI.C.4. CHROMATOGRAM OF 1.90 ug/ml STANDARD ANALYSIS ON DAY 2



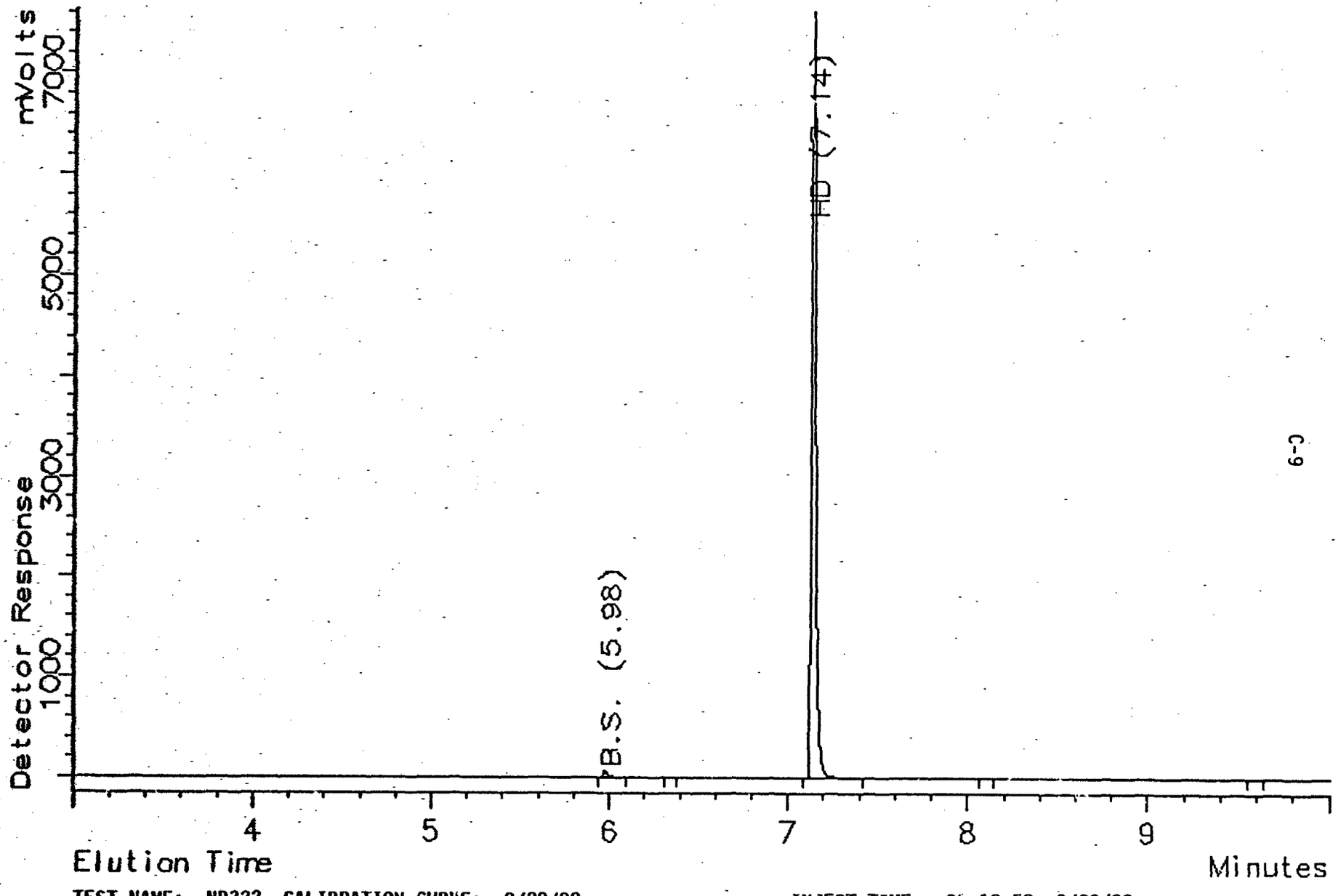
C-8

TEST NAME: NP316 CALIBRATION CURVE: 9/29/88
GC0300

INSTRUMENT: 1

INJECT TIME: 20:23:53 9/29/88

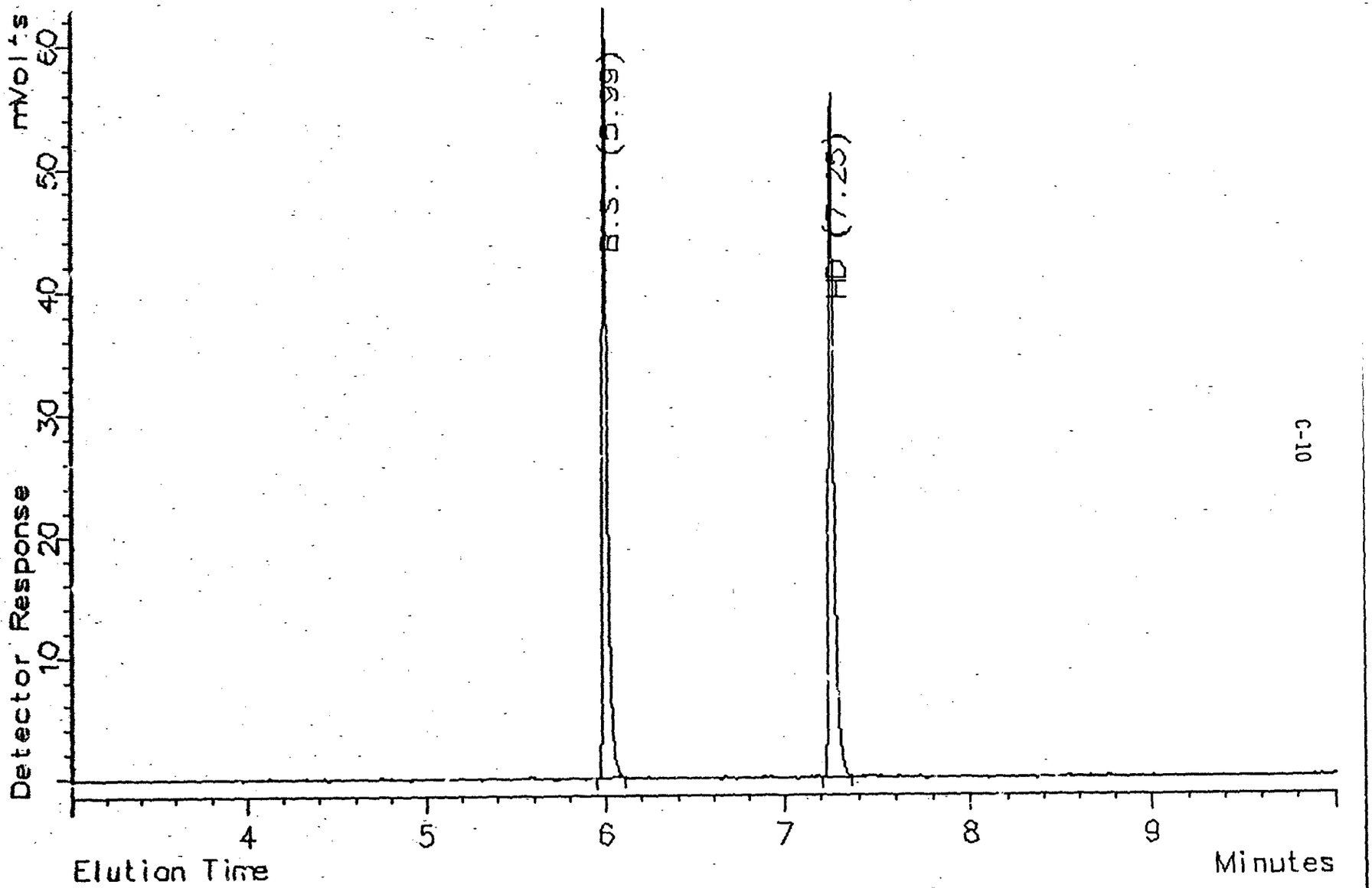
FIGURE XI.C.5. CHROMATOGRAM OF 19.0 ug/ml STANDARD ANALYSIS ON DAY 2



C-9

TEST NAME: NP322 CALIBRATION CURVE: 9/29/88 INJECT TIME: 2?.12:58 9/29/88
GC0300 INSTRUMENT: 1

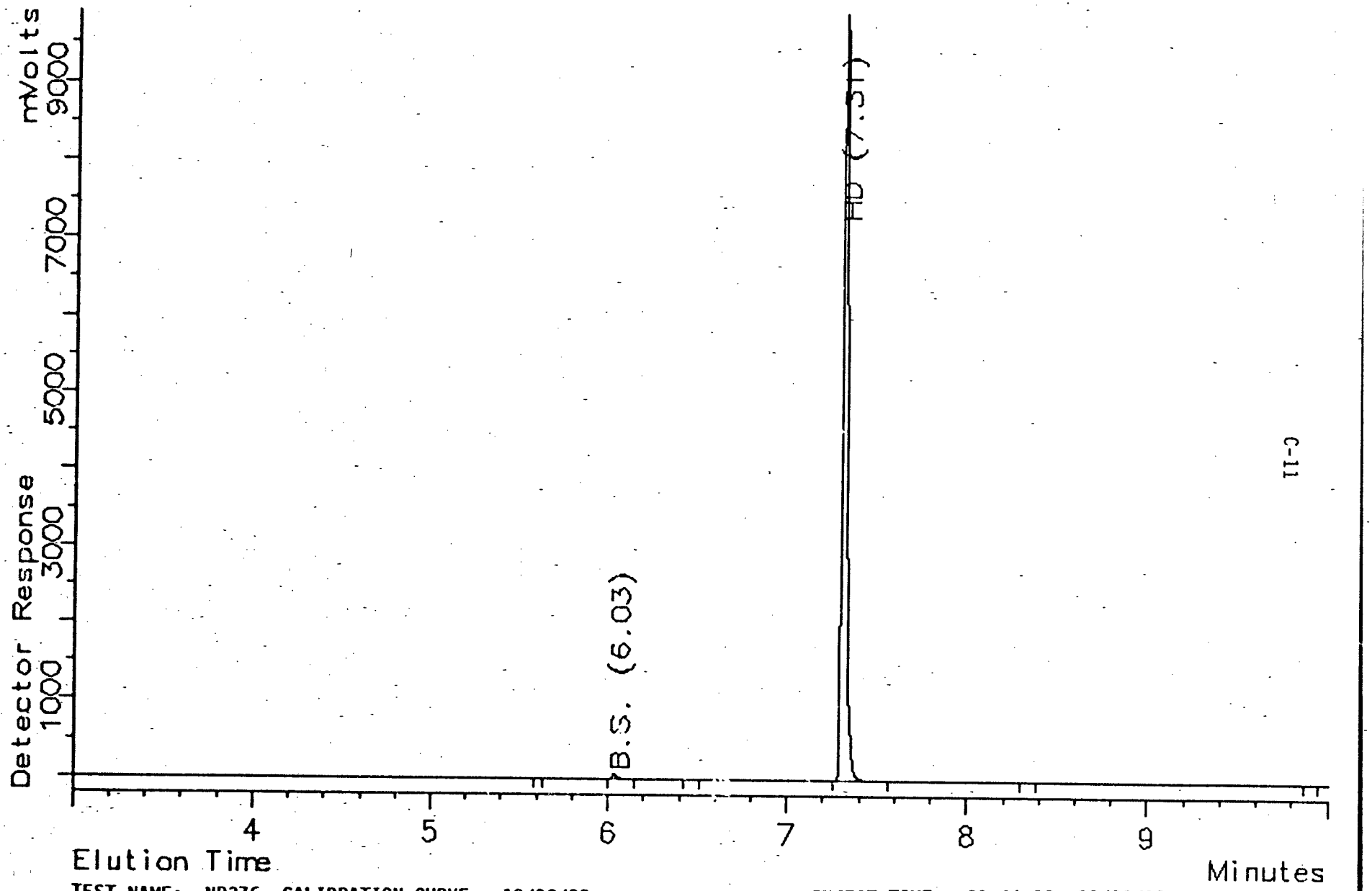
FIGURE XI.C.6. CHROMATOGRAM OF 1.90 ug/ml STANDARD ANALYSIS ON DAY 3



C-10

TEST NAME: NP370 CALIBRATION CURVE: 10/03/88 INJECT TIME: 19:53:27 10/03/88
GC0300 INSTRUMENT: 1

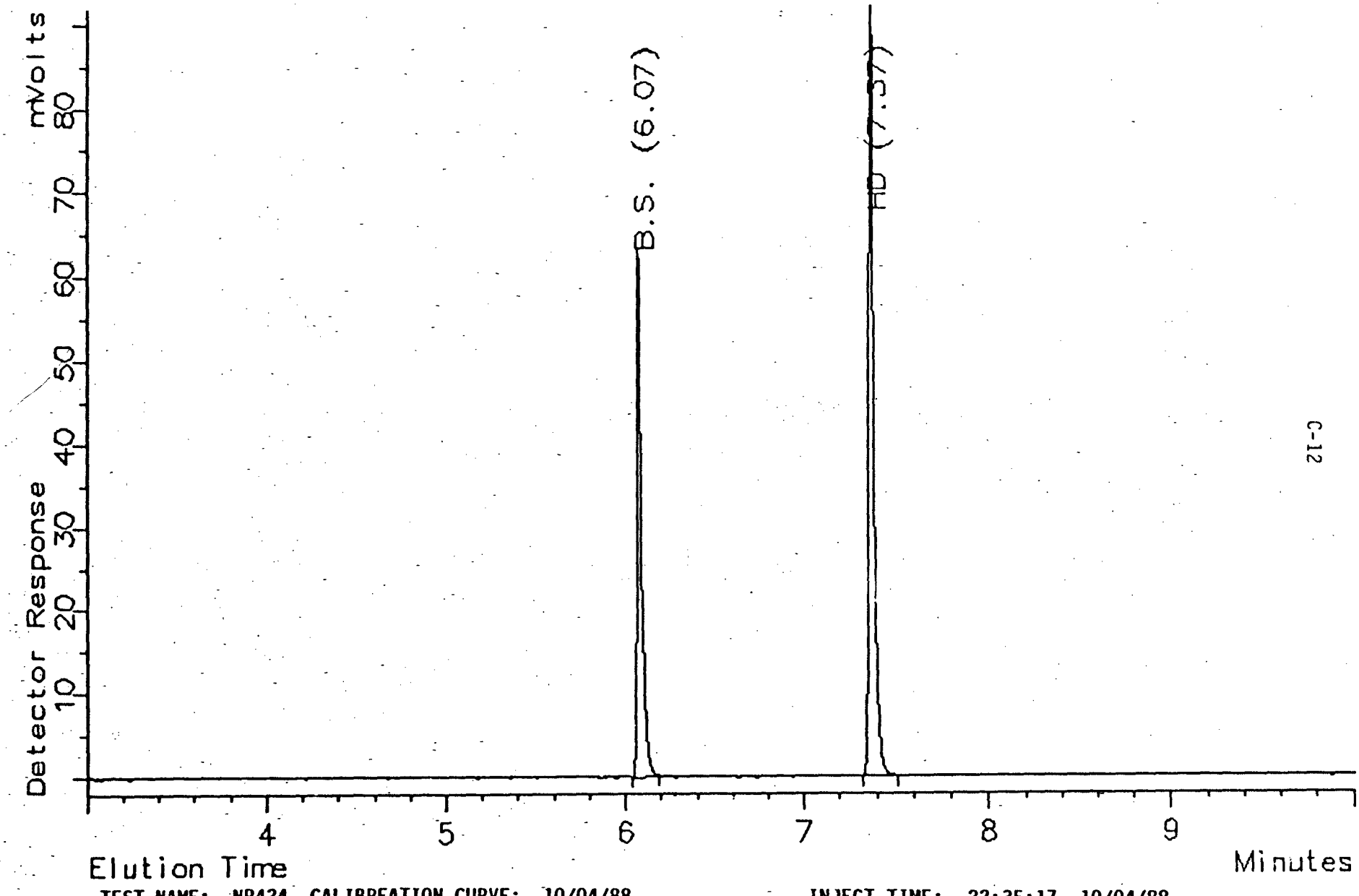
FIGURE XI.C.7. CHROMATOGRAM OF 19.0 ug/ml STANDARD ANALYSIS ON DAY 3



C-11

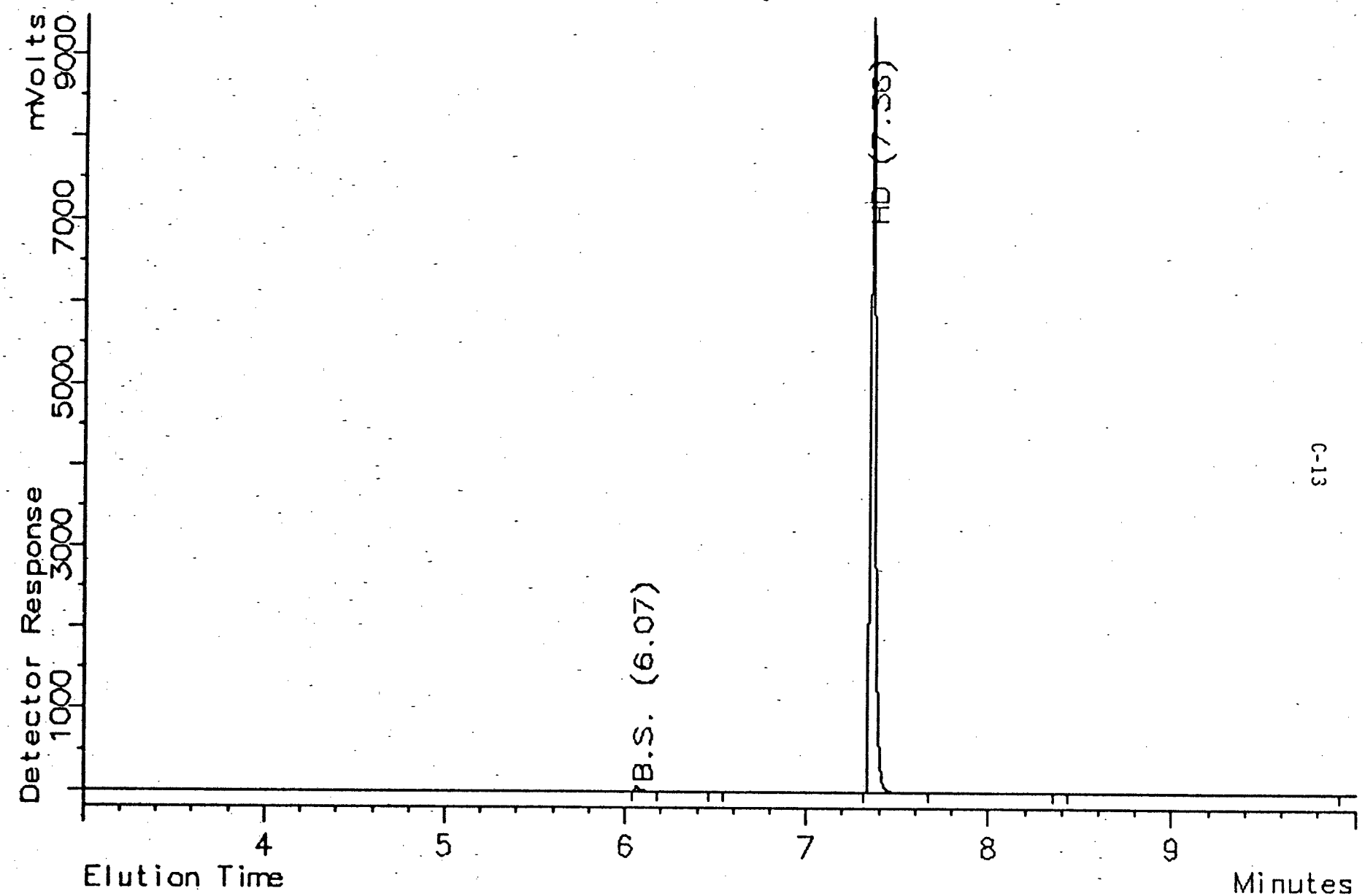
TEST NAME: NP376 CALIBRATION CURVE: 10/03/88 INJECT TIME: 21:41:08 10/03/88
GC0300 INSTRUMENT: 1

FIGURE XI.C.8. CHROMATOGRAM OF 1.90 ug/ml STANDARD ANALYSIS ON DAY 4



TEST NAME: NP424 CALIBREATION CURVE: 10/04/88 INJECT TIME: 22:35:17 10/04/88
GC0300 INSTRUMENT: 1

FIGURE XI.C.9. CHROMATOGRAM OF 19.0 ug/ml STANDARD ANALYSIS ON DAY 4



C-13

TEST NAME: NP430 CALIBRATION CURVE: 10/04/88 INJECT TIME: 0:24:21 10/05/88
GC0300 INSTRUMENT: 1

END

FILMED

DATE: 2-92

DTIC